Understanding and Mitigating the Effects of Stable Dodecahydro-closo-dodecaborate Intermediates on Hydrogen-Storage Reactions

James L. White,† Rebecca J. Newhouse,‡ Jin Z. Zhang,§ Terrence J. Udovic,‡ and Vitalie Stavila§†

†Sandia National Laboratories, Livermore, California 94551, United States
‡Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064, United States
§NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: Alkali metal borohydrides can reversibly store hydrogen; however, the materials display poor cyclability, oftentimes linked to the occurrence of stable closo-polyborate intermediate species. In an effort to understand the role of such intermediates on the hydrogen storage properties of metal borohydrides, several alkali metal dodecahydro-closo-dodecaborate salts were isolated in anhydrous form and characterized by diffraction and spectroscopic techniques. Mixtures of Li$_2$B$_{12}$H$_{12}$, Na$_2$B$_{12}$H$_{12}$, and K$_2$B$_{12}$H$_{12}$ with the corresponding alkali metal hydrides were subjected to hydrogenation conditions known to favor partial or full reversibility in metal borohydrides. The stoichiometric mixtures of MH and M$_2$B$_{12}$H$_{12}$ salts form the corresponding metal borohydrides MBH$_4$ (M = Li, Na, K) in almost quantitative yield at 100 MPa H$_2$ and 500 °C. In addition, stoichiometric mixtures of Li$_3$B$_{12}$H$_{12}$ and MgH$_2$ were found to form MgB$_2$ at 500 °C and above upon desorption in vacuum. The two destabilization strategies outlined above suggest that metal polyhydro-closo-polyborate species can be converted into the corresponding metal borohydrides or borides, albeit under rather harsh conditions of hydrogen pressure and temperature.

1. INTRODUCTION

Light-metal borohydrides are attractive candidates for solid-state hydrogen storage due to their high weight percentages of hydrogen, up to 18.4% for LiBH$_4$. Unfortunately, the total release of hydrogen as well as the complete reversal of the process have proven difficult, leading to high reaction temperatures and slow rates. One of the major obstacles to reversibility is the formation of pseudoaromatic closo-borate intermediates, including M$_6$B$_{10}$H$_{10}$ and M$_3$B$_{12}$H$_{12}$ (n = 1 for alkaline-earth metals, n = 2 for alkali metals), which act as thermodynamic and kinetic sinks. Destabilizing these polyboron hydride species can alter the reaction pathways and allow for greater hydrogenation reversibility.

Dodecahydro-closo-dodecaborate compounds were first theoretically predicted in 1955 by Longuet-Higgins and Roberts on the basis of MO-LCAO calculations, suggesting that a borane with an icosahedral $I_5$ symmetry would only be stable as a dianion. This stimulated a flurry of experimental research, and, in 1960, Pitochelli and Hawthorne reported the synthesis of the first [B$_2$H$_4$]$_2$ 2− compound, [Et$_3$NH][B$_2$H$_4$], obtained in small yield as a byproduct of the reaction of 2-iododecaborane and triethylamine in benzene. The existence of such compounds and their chemical properties are determined by the presence of delocalized electrons and the aromatic character of the chemical bonding. The pseudoaromatic nature of the closo-borates of general formula [B$_n$H$_{2n-}$]$_{2n-}$ is responsible for their unique properties compared with nido-, hypno-, arachno-, or klado-boranes: high thermal and kinetic stability, salt-like behavior, and tendency to undergo B−H substitution rather than B−B bond-breaking reactions.

The occurrence of [B$_2$H$_4$]$_2$ 2− species among the decomposition products of metal borohydrides is not surprising, as multiple preparative synthetic approaches toward [B$_2$H$_4$]$_2$ 2− and [B$_n$H$_{2n}$]$_{2n-}$ species involve borohydride compounds as starting materials. A number of efforts to enhance the dehydrogenation of metal borohydrides have been undertaken, beginning with Vajo et al., who employed MgH$_2$ to destabilize LiBH$_4$. A variety of additives, particularly alkaline earth and transition metals and metal hydrides, have been found to be effective in partially or fully dehydrodrying borohydride materials. Less work has been done on destabilizing the closo-borate intermediates themselves. Ozolins et al. employed first-principles DFT calculations to predict several decomposition reactions involving Li, Mg, and Ca borohydrides and [B$_2$H$_4$]$_2$ 2− salts, the latter of which are formed in the first part of a two-step decomposition pathway. However, only one of the predicted close-borate reactions, the dehydrogenation of CaB$_{12}$H$_{12}$ with CaH$_2$, has been investigated.
experimentally thus far. The rehydrogenation of closo-borates, although occasionally attempted, has not met with success at all, even though complete reversibility frequently requires the accessibility of both processes. While closo-borates are often, but not always, detected in borohydride decomposition reactions, a variety of other B\(_2\)H\(_x\) intermediates have also been shown to form. However, of these compounds, the [B\(_2\)H\(_{12}\)]\(^{2-}\) dianion represents the most extreme case of thermal and kinetic stability due to its pseudooaromatic nature compared with the more open and reactive nido-, hypho-, arachno-, and klado-boranes.

In this work, reactions I–IV, which involve either dehydrogenation (I–III) or dehydrogenation (IV) of [B\(_2\)H\(_{12}\)]\(^{2-}\) salts, were conducted. The alkali closo-borates were fully dehydrogenated to the borohydrides, unlike the CaB\(_2\)H\(_{12}\) previously studied. In addition, Li\(_2\)B\(_2\)H\(_{12}\) was destabilized by MgH\(_2\), forming MgB\(_2\). These studies reveal that the stability of the closo-borate salts can, in principle, be overcome and lead to greater effective hydrogen capacities for metal borohydrides.

Hydrogenation:
\[
\begin{align*}
&\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH} + 13\text{H}_2 \rightarrow 2\text{LiBH}_4 & (I) \\
&\text{Na}_2\text{B}_{12}\text{H}_{12} + 10\text{NaH} + 13\text{H}_2 \rightarrow 2\text{NaBH}_4 & (II) \\
&\text{K}_2\text{B}_{12}\text{H}_{12} + 10\text{KH} + 13\text{H}_2 \rightarrow 2\text{KBH}_4 & (III) \\
&\text{Dehydrogenation:} & (IV)
\end{align*}
\]

\[
\begin{align*}
&\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2 \rightarrow 6\text{MgB}_2 + 2\text{LiH} + 11\text{H}_2 
\end{align*}
\]

2. EXPERIMENTAL METHODS

2.1. Synthesis of M\(_2\)B\(_{12}\)H\(_{12}\) Compounds (M = Li, Na, K).

The preparation of the dodecahydro-closo-dodecaborate compounds was performed as had been previously reported. Initially, 4.5 g Cs\(_2\)B\(_{12}\)H\(_{12}\) (Sigma-Aldrich) was added to 75 mL of Milli-Q water (18 M\(\Omega\)), and the mixture was heated almost to boiling to dissolve the salt. The hot solution was eluted with warm Milli-Q water through an Amberlite IR-120 column to ensure complete conversion. The hot solution was then passed through another protonated Amberlite IR-120 column to elute the acid was titrated to a pH of 7 with the hydroxide or the base was used in the attenuated total reflection infrared (ATR) mode. Following collection of the patterns, the background was subtracted to remove the signal from the amorphous glass.

Raman spectra were collected using a 532 nm laser with a power of 0.5 mW directed through an Acton Spectropro-275 monochromator/spectrograph with a 600 grooves/mm grating to a liquid-nitrogen-cooled Spec-10 CCD detector. Fourier transform infrared (FTIR) spectra were obtained using either a Varian 800 or an Agilent Cary 630 FTIR spectrometer. Both were used in the attenuated total reflectance (ATR) mode. Neutron vibrational spectroscopy (NVS) measurements were made at temperatures of 4 K at the NIST Center for Neutron Research using the BT-4 Filter-Analyzer Neutron Spectrometer (FANS) with a Cu(220) monochromator and 20 min of arc for the pre- and post-comonochromator collimations. Solid-state nuclear magnetic resonance spectra of the \(^1\)H and \(^11\)B nuclides were gathered by Spectral Data Services on a 360 MHz spectrometer with rotation rates of 10.0 kHz. For all figures, standard uncertainties are commensurate with the observed scatter in the data if not explicitly designated by vertical error bars.

3. RESULTS AND DISCUSSION

3.1. Hydrogenation of M\(_2\)B\(_{12}\)H\(_{12}\) Compounds. The powder x-ray diffraction (XRD) patterns of the synthesized and dried Li\(_2\)B\(_2\)H\(_{12}\), Na\(_2\)B\(_2\)H\(_{12}\), and K\(_2\)B\(_2\)H\(_{12}\) (Figure 1) match well with those previously reported, indicating that these compounds are in the cubic Pa\(_3\), monoclinic P2\(_1\)/n, and cubic Fm\(_3\) space groups, respectively. In addition, the FTIR spectra of each (Figure S1) and the absence of the O–H stretching band from water indicate that the samples were dried and possessed no water of hydration. The presence of water is detrimental, as alkaline and alkaline-earth metal hydrides irreversibly react with H\(_2\)O to form hydroxides and other oxidized species. For all three M\(_2\)B\(_{12}\)H\(_{12}\) salts, the strong B–H stretching mode between 2500
and 2470 cm\(^{-1}\) and the B–H bending mode near 1080 cm\(^{-1}\) confirm the presence of the \(\text{B}_2\text{H}_{12}^-\) anion.\(^{15}\)

A pellet of milled \(\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH}\), before and after exposure to 100 MPa \(\text{H}_2\) at 500 °C, is shown in Figure 2. After heating under high hydrogen pressure, the pellet was observed to spread out and fill the bottom of the vessel, indicating the liquefaction of the material during the course of the reaction, followed by resolidification upon cooling back to room temperature. Similar behavior was found for the sodium mixture, while the potassium pellet merely deformed slightly. While the \(\text{M}_2\text{B}_{12}\text{H}_{12}\) compounds persist as solids above 500 °C,\(^{15}\) the borohydrides have melting points of 268, 400, and 585 °C for Li, Na, and K, respectively.\(^{39}\)

The nearly complete conversion of ball-milled \(\text{M}_2\text{B}_{12}\text{H}_{12}\) and MH to MBH\(_4\) under high-pressure hydrogen (100 MPa) was confirmed with various characterization techniques. The powder XRD patterns (Figure 3) of each of the reaction product mixtures showed primarily crystalline MBH\(_4\) in each, with small but detectable quantities of \(\text{M}_2\text{B}_{12}\text{H}_{12}\) and MH. These are likely simply unreacted species because the equilibrium pressure for the \(12\text{LiBH}_4 \Leftrightarrow \text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH} + 13\text{H}_2\) reaction based on calculations from Ozolins et al. is much lower than the experimental conditions, at only \(~120\) bar.\(^{27}\) Kinetic barriers, including slow diffusion of solid-state reactants, likely hindered the completion of the reaction. Rietveld refinement was employed to characterize the relative amounts of each crystalline phase. In all three cases, the amount of borohydride was >80% (Table S1). The lattice parameter of the KBH\(_4\) phase, 6.7249(2) Å, did not exactly match that of the database pattern plotted but was within the range of the several refinements catalogued (Table S2). Ball-milling the starting \(\text{M}_2\text{B}_{12}\text{H}_{12}/\text{MH}\) mixtures increases the borohydride yield, likely due to an improved contact between the hydride and closo-borate crystallites, as found for other hydride systems.\(^{40}\)

XRD, of course, does not take into account amorphous phases, including some intermediate boron-hydride species reported in the dehydrogenation of borohydrides.\(^{4,9,15}\) For the detection of such possible products, NVS (Figure 4) and Raman (Figure 5) of the final reacted materials were compared with the pure individual starting materials and expected borohydride products. NVS is a summation of all hydrogen scattering, regardless of the species’ crystallinity. The NVS comparison spectra also clearly indicate the conversion to borohydride. The borohydride libration peaks (52 meV for \(\text{LiBH}_4\),\(^{41}\) 44 meV for \(\text{NaBH}_4\), and 42 meV for \(\text{KBH}_4\)\(^{42}\)) are readily apparent in the spectra of the corresponding resulting materials. Although the lower intensity combination bands at intermediate energies are less visible, the higher energy bending modes (134 and 158 meV for \(\text{LiBH}_4\), 140 and 159 meV for \(\text{NaBH}_4\), and 140 and 156 meV for \(\text{KBH}_4\)\(^{43}\)) are evident in the product spectra. The peaks for the MH\(^{14}\) and \(\text{M}_2\text{B}_{12}\text{H}_{12}\)\(^{15}\) species are not discernible above the borohydride combination bands, indicating the presence of, at most, only low levels of those compounds, and no peaks corresponding to other intermediate phases such as \(\text{Li}_2\text{B}_{10}\text{H}_{10}\) or \(\text{Na}_2\text{B}_{10}\text{H}_{10}\)\(^{46,47}\) were present above the detection limit either.

Raman spectroscopy is also sensitive to B–H vibrations and would detect partially hydrogenated species. However, only \([\text{BH}_4]^-\) and \([\text{B}_{12}\text{H}_{12}]^{2-}\) peaks are detected, with no other signals corresponding to \([\text{B}_{10}\text{H}_{10}]^{2-}\) compounds or other boron hydrides.\(^{48}\) In the Na Raman spectra, for example, peaks at 589 and 756 cm\(^{-1}\) corresponding to B–H bending modes are seen in both the \(\text{Na}_2\text{B}_{12}\text{H}_{12}\) starting material as well as the sample after the high-pressure experiment. NaH does not scatter strongly and therefore does not show any distinguishable features that can be recognized in the spectrum of the reacted sample. However, accounting for differences in scattering intensity and the possibility of heterogeneity in the sample, the

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Figure 1. X-ray diffraction patterns of \(\text{Li}_2\text{B}_{12}\text{H}_{12}\), \(\text{Na}_2\text{B}_{12}\text{H}_{12}\), and \(\text{K}_2\text{B}_{12}\text{H}_{12}\), with their corresponding database patterns shown for comparison.

Figure 2. Photograph of \(\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH}\) in the reaction vessel (a) prior to and (b) after subjection to 100 MPa \(\text{H}_2\) at 500 °C.
borohydride species is the majority phase in each of the product mixtures. The presence of highly hydrogenated B−H species in the hydrogenated Li_{2}B_{12}H_{12}+10LiH sample was further confirmed using temperature-programmed desorption. The dehydrating behavior upon heating the regenerated Li_{2}B_{12}H_{12}+10LiH material upon heating from room temperature to 700 °C resembles that of an authentic sample of lithium borohydride (Figure S2), although the amount of hydrogen released is only 12.5 wt % compared with 14.1 wt % for pure LiBH_{4}.

Magic-angle spinning solid-state nuclear magnetic resonance spectroscopy (Figure S3) was also performed on the three posthydrogenated samples. Each of the ^{11}B spectra, referenced to BF_{3}·OEt_{2}, had a large peak corresponding to borohydride: −41.5 ppm for LiBH_{4}, −42.2 ppm for NaBH_{4}, and −38.3 ppm for KBH_{4}, matching the values reported in the literature.4,9,10,49 The slight differences in peak position result from minor variations in the chemical environment of the [BH_{4}]^{−} anion. Of the three reaction products, only the potassium mixture had a well-defined peak at −15.4 ppm, which corresponds to the [B_{12}H_{12}]^{2−} anion, although the XRD pattern of the lithium mixture also showed detectable amounts of the Li_{2}B_{12}H_{12} phase. The ^{1}H MAS spectra reveal (Figure S3) broad peaks centered at 0.2 ppm for the [BH_{4}]^{−} ion. The Li and Na ^{1}H spectra also possess smaller, sharper peaks that may correspond to the metal hydrides, [B_{12}H_{12}]^{2−} species, or other phases that are amorphous and not detected by XRD.

3.2. Dehydrogenation of closo-Borates. In previous studies, the alkali dodecahydro-closo-dodecaborates have been found to be too stable for complete dehydrogenation, both on their own and with their corresponding metal hydrides.2,31 However, it has been theorized that B_{12}H_{12}^{2−} compounds, with both alkali and alkaline earth counterions, can be destabilized using alkaline earth metals or metal hydrides, from which strongly bound borides are produced.27 Previous work has already shown success with CaB_{12}H_{12} mixed with CaH_{2}, yielding crystalline CaB_{6} and hydrogen upon heating.28 In this study, Li_{2}B_{12}H_{12} was dehydrogenated using MgH_{2} as a destabilizing agent to form MgB_{2}.

The Li_{2}B_{12}H_{12} described above for the hydrogenation experiments was also employed for dehydrogenation in the presence of 6 equiv of MgH_{2}. Reaction IV, in which MgH_{2} is employed to destabilize Li_{2}B_{12}H_{12}, has a theoretical reaction temperature of 215 °C, whereas Li_{2}B_{12}H_{12} alone begins to decompose above 250 °C while retaining the B_{12} icosahedral cores.15,31 The Li_{2}B_{12}H_{12} and MgH_{2} powders were ground and then ballmilled together for 1 h, followed by pressing into pellets. The dehydrogenation reaction was performed at several temperatures under vacuum for 18 h. Metallic Mg was formed from the desorption of the MgH_{2}, as previously observed in the LiBH_{4}−2MgH_{2} system.50 However, no MgB_{2} was observed below 500 °C. By 700 °C, almost all of the in-situ-generated Mg had been consumed, yielding primarily crystalline MgB_{2}, indicating the dissociation rather than polymerization of the B_{12} icosahedra but also some MgO (Figure 6). The source of oxygen is unclear, but it might originate from reaction with small amounts of adsorbed water or oxygen on the walls of the reaction vessel. No Li-containing species were observed by XRD after the thermal treatment, possibly due to the high volatility of Li and the decomposition of Li_{2}B_{12}H_{12} to amorphous species at 500 °C and above, as previously observed.15,31 Experiments with metallic magnesium instead of MgH_{2} as the starting material were also attempted to confirm the reaction of Mg rather than the hydride; however, the soft metal did not mix with the Li_{2}B_{12}H_{12} salt during milling and thus would not react comparably.

Hydrogen desorption from ball-milled Li_{2}B_{12}H_{12} + 6MgH_{2} was measured in a Sieverts apparatus up to a final temperature of 25728

Figure 3. Posthydrogenation powder diffraction patterns of (a) Li_{2}B_{12}H_{12} + 10LiH (b) Na_{2}B_{12}H_{12} + 10NaH, and (c) K_{2}B_{12}H_{12} + 10KH. Peaks corresponding to component phases are shown in green (MBH_{4}), blue (M_{2}B_{12}H_{12}), and red (MH).
The initial stage of desorption did not occur until the measured temperature was above 380 °C. The desorption achieved its maximum rate after reaching 600 °C and tapered off after about 1 h at that temperature until finally plateauing at 5.9 wt % H, 76.5% of the 7.7 wt % theoretical capacity of the Li₂B₁₂H₁₂ + 6MgH₂ mixture. This amount of released hydrogen is slightly above the 5.1 wt % (66% of theoretical) at 700 °C reported by He et al. for pure Li₂B₁₂H₁₂, although the latter occurs through the irreversible formation of B₁₂H₉ polymers.31 The fully hydrogenated mixture, 2LiBH₄ + MgH₂, had an observed hydrogen capacity of 8 to 9 wt % (55−60% of the theoretical hydrogen content) at 425−450 °C and of 600 °C (Figure 7). The initial stage of desorption did not occur until the measured temperature was above 380 °C. The desorption achieved its maximum rate after reaching 600 °C and tapered off after about 1 h at that temperature until finally plateauing at 5.9 wt % H, 76.5% of the 7.7 wt % theoretical capacity of the Li₂B₁₂H₁₂ + 6MgH₂ mixture. This amount of released hydrogen is slightly above the 5.1 wt % (66% of theoretical) at 700 °C reported by He et al. for pure Li₂B₁₂H₁₂, although the latter occurs through the irreversible formation of B₁₂H₉ polymers.31 The fully hydrogenated mixture, 2LiBH₄ + MgH₂, had an observed hydrogen capacity of 8 to 9 wt % (55−60% of the theoretical hydrogen content) at 425−450 °C and

Figure 4. Neutron vibrational spectra of the MH (red), MₓB₁₂H₁₂ (blue), MBH₄ (green), and the hydrogenated reaction mixtures (black) of (a) Li, (b) Na, and (c) K. Error bars represent one standard deviation. Spectra are vertically offset for clarity.

Figure 5. Raman spectra of the (a) Li, (b) Na, and (c) K systems. Spectra in black are from the reaction mixtures, whereas those in green, blue, and red correspond to the pure MBH₄, MₓB₁₂H₁₂, and MH materials, respectively. Spectra are vertically offset for clarity.

Figure 6. XRD patterns of the Li₂B₁₂H₁₂ + 6MgH₂ ball-milled mixtures heated to 500, 600, and 700 °C with standard patterns for Mg (orange), MgO (magenta), and MgB₂ (cyan).

Figure 7. Temperature-programmed desorption of ball-milled Li₂B₁₂H₁₂ + 6MgH₂ during heating to 600 °C. The blue curve with markers indicates the wt % H released, while the dotted red curve shows the temperature profile.
Although further investigations are needed to determine the thermodynamically predicted temperature indicates that significant kinetic barriers exist that inhibit hydrogen release. Ozelins et al. hypothesized that MgH₂ disrupts the pseudoaromatic B₁₂H₁₂⁻ ion and enables the removal of hydrogen from that species, even when Li₂B₁₂H₁₂ is formed in situ from the dehydrogenation of LiBH₄. However, experimental work by Vajo et al. demonstrated the conversion of LiBH₄ and MgH₂ to LiH and MgB₂ at only 450 °C, suggesting that the Li₂B₁₂H₁₂ intermediate is circumvented, rather than merely destabilized, by the presence of MgH₂ during LiBH₄ decomposition.

4. CONCLUSIONS

The alkali and alkaline earth dodecaborate-containing breakdown products and intermediates have been implicated as highly stable intermediates that prevent the reversible dehydrogenation of borohydrides, which are otherwise quite promising hydrogen storage materials. Herein we show that metal hydrides can have a destabilizing effect on [B₁₂H₁₂]²⁻ compounds. At 100 MPa H₂ and 500 °C, Li₂B₁₂H₁₂, Na₂B₁₂H₁₂, and K₂B₁₂H₁₂ can be hydrogenated almost quantitatively into the respective alkali borohydrides in the presence of metal hydrides. The high hydrogen pressure hydrogenation could be a promising route to mitigate the occurrence of intermediate boron hydrides in metal borohydrides, especially in the context of the 35 and 70 MPa hydrogen fueling infrastructure currently being deployed. In addition, this route represents an interesting synthetic approach to metal borohydrides. The transformations of [B₁₂H₁₂]²⁻ compounds into the corresponding borohydrides were confirmed with a wide variety of analytical and spectroscopic techniques. In addition, dehydrogenation of Li₂B₁₂H₁₂ was examined utilizing MgH₂ as a destabilizing agent to form MgB₂ at 500 °C and above. The unwillingness of [B₁₂H₁₂]²⁻ to undergo hydrogen release or absorption reactions under milder conditions is clearly associated with the high stability of the B–B bonds in pseudoaromatic dodecaborate-closo-dodecaborate anionic cages. Although further investigations are needed to determine the routes and mechanisms by which B₁₂H₁₂⁻ and other intermediate boron hydride species are broken down, this study clearly highlights a possible mitigation of this problem by using destabilization approaches, which modify the reaction pathways and favor the hydrogen cycling reactions.

ASSOCIATED CONTENT

Supporting Information

Infrared spectra of dried M₂B₁₂H₁₂ salts, calculated mass fractions postreactions, KH₄B₄, lattice parameters, and solid-state NMR spectra. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: vnstavila@sandia.gov.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(34) The mention of all commercial suppliers in this paper is for clarity and does not imply the recommendation or endorsement of these suppliers by NIST.
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†Sandia National Laboratories, Livermore, California 94551
‡Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA95064
§NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899

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Figure S1. Infrared spectra of dried Li$_2$B$_{12}$H$_{12}$, Na$_2$B$_{12}$H$_{12}$, and K$_2$B$_{12}$H$_{12}$. 
Table S1. Mass percentages of *closo*-borate, metal hydride, and metal borohydride in each of the alkali metal systems after hydrogenation, as determined by Rietveld refinement of the XRD patterns shown in Figure 3.

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<td>M2B12H12</td>
<td>MH</td>
<td>MBH4</td>
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<td>K</td>
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Table S2. Lattice parameters of database *Fm*3*m* KBH4 patterns and refined parameter of KBH4 in the reaction mixture.

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Figure S2. Temperature programmed desorption of hydrogenated Li$_2$B$_{12}$H$_{12}$+10LiH (blue curve) and commercial LiBH$_4$ (green curve) heating up from room temperature to about 700 °C. The red curve indicates the temperature profile.
Figure S3. MAS solid-state (a) $^{11}$B and (b) $^1$H NMR spectra of the post-reaction mixtures, performed at spin rates of 10 kHz. In the $^{11}$B spectrum, a green circle denotes the BH$_4^-$ peak (around -38 to -42 ppm) and a blue triangle indicates the B$_{12}$H$_{12}^{2-}$ peak in the K spectrum at -16 ppm. Asterisks denote the spinning sidebands. The inset shows a more detailed view near the B$_{12}$H$_{12}^{2-}$ peak.